Les atomes de carbone et d'azote de l'ion pentanediammonium-1,5 sont tous situés dans le plan $x = 0$ ou dans le plan $x = \frac{1}{2}$. En outre, cet ion admet, pour plan de symétrie, le plan $y = 0$ et, pour axe de symétrie, l'axe Oz ou l'axe intersection des plans $y = 0$ et $x = \frac{1}{2}$. Les longueurs des liaisons C—C [1,501 (6) et 1,512 (5) Å] et de la liaison C(2)—N(1) [1,480 (5) Å] sont compatibles, compte tenu des incertitudes, avec les longueurs trouvées pour les mêmes liaisons dans le chlorure de propanediammonium-1,3 (Brisson & Brisse, 1982) [C—C: 1,515 (4), C—N: 1,484 (4) Å] ou dans l'hydrogénophosphate de putrescinium dihydraté (Jaskólski, Alejska & Wiewiórowski, 1986) [C—C: 1,511 (5), C—N: 1,488 (1) Å]. Il en est de même pour les angles N—C—C et C—C—C (Tableau 2). Dans le dernier composé cité, leurs homologues mesurent respectivement 113 (1) et 111,7 (8)°.

La Fig. 1 montre que les cations $[C_5H_{16}N_2]^{2+}$ forment des couches qui zigzaguent au voisinage des plans $z = \pm\frac{1}{8}$ et $z = \pm\frac{3}{8}$. Deux couches consécutives de cations sont séparées tantôt par une couche d'anions Cl^-, tantôt par une couche d'anions $[PtCl_6]^{2-}$. Les premiers sont situés dans les plans $z = \pm\frac{1}{4}$ et les seconds ont pour positions moyennes les plans $z = 0$ et $z = \frac{1}{2}$.

La cohésion de la structure fait intervenir les liaisons hydrogène N(1)—H(N1)···Cl(1^{iii}) [3,173 (2) Å, 168°] [(iii): $1-x$, y, z] et N(1)—H′(N1)···Cl(3^{iv}) [3,274 (3) Å, 137°] [(iv): $\frac{1}{2}+x$, $\frac{1}{2}+y$, z].

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Structure of Bis(2-amino-5-methylpyridinium) Tetrachlorocuprate(II) and Bis(2-amino-5-methylpyridinium) Tetrabromocuprate(II)

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Abstract. $2C_6H_9N_2^+.CuCl_4^{2-}$, $M_r = 423{\cdot}7$, monoclinic, $C2/c$, $a = 13{\cdot}377$ (4), $b = 8{\cdot}344$ (3), $c = 15{\cdot}941$ (4) Å, $\beta = 93{\cdot}38$ (2)°, $V = 1776{\cdot}2$ (1) Å^3, $Z = 4$, $D_x = 1{\cdot}58$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 18{\cdot}30$ cm^{-1}, $F(000) = 860$, $T = 293$ K, final $R = 0{\cdot}0545$ for 701 unique observed reflections. The structure consists of discrete $CuCl_4^{2-}$ anions and 2-amino-5-methylpyridinium cations. The $CuCl_4^{2-}$ ions lie on a twofold axis and have approximate D_{2d} symmetry with Cu—Cl(average) = 2·240 Å and '*trans*' Cl—Cu—Cl(average) = 140·0°. $2C_6H_9N_2^+.CuBr_4^{2-}$, $M_r = 601{\cdot}5$, monoclinic, $C2/c$, $a = 13{\cdot}715$ (2), $b = 8{\cdot}7162$ (2), $c = 16{\cdot}013$ (4) Å, $\beta = 93{\cdot}79$ (2)°, $V = 1910{\cdot}1$ (6) Å^3, $Z = 4$, $D_x = 2{\cdot}09$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 94{\cdot}46$ cm^{-1}, $F(000) = 1148$, $T = 293$ K, final $R = 0{\cdot}0521$ for 658 unique observed reflections. The tetrabromide structure is isomorphous with the tetrachloride structure. Cu—Br(average) = 2·376 Å and *trans* Br—Cu—Br(average) = 137·1°.

Introduction. A central interest in this laboratory has been the study of the magnetic and structural characteristics of quasi-planar $Cu_mX_{2m+2}^{2-}$ and $Cu_mX_{2m}L_2$ ($X = Cl^-$ or Br^-) oligomers (Geiser, Willett, Lindbeck & Emerson, 1986; O'Brien, Gaura, Landee, Ramakrishna & Willett. 1987). These form bibridged species, which are essentially fragments of the anhydrous $CuCl_2$ (Wells, 1947) and $CuBr_2$ (Helmholz, 1947) structures. It has been found (Grigereit, 1986) that the 2-amino-*n*-methylpyridinium cation, where $n = 3$, 4, 5

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or 6, can form salts which contain $Cu_mX^{2-}_{2m+2}$ anions ($m = 3$ or 4). In the preparation of the $n = 5$ salt, a yellow crystalline impurity was formed in addition to the desired oligomeric salt. In order to devise an improved method for obtaining pure samples of the oligomeric salt for magnetic studies, a crystal structure analysis of the impurity was performed. The results indicated that the impurity had the formulation (2-amino-5-methylpyridinium)$_2$CuCl$_4$.

A series of copper bromide salts analogous to the known copper chlorides have been sought with the 2-amino-*n*-methylpyridinium anions. In an attempt to make the 2-amino-5-methylpyridinium copper bromide oligomer the only crystals collected turned out to be the tetrabromide.

Experimental. For the tetrachloride salt, small yellow plate-like crystals separated out as a minor impurity upon crystallization of a solution of 2-amino-5-methylpyridinium hydrochloride and anhydrous copper(II) chloride (approximately 1:4 stoichiometry) in *n*-propyl alcohol which yielded primarily fine straw-colored needles of $(C_6N_2H_9)_2Cu_3Cl_8$. A crystal approximately 0·1 × 0·2 × 0·2 mm was selected for data collection. Data were collected with an ω scan on a Nicolet *R*3*m*/*E* diffractometer system with Mo *K*α radiation and a graphite monochromator (Campana, Shepherd & Litchman, 1980). Agreement between equivalent reflections: $R = 0{\cdot}0145$. The monoclinic cell and orientation matrix were defined by least-squares refinement of 25 reflections in the 2θ range 20–22°. Space group *C*2/*c* (extinctions: *hkl*, *h* + *k* odd; *h*0*l*, *l* odd). Empirical ψ scan absorption corrections ($\mu = 18{\cdot}30$ cm^{-1}) assuming an ellipsoidal-shaped crystal (minimum transmission = 0·67, maximum transmission = 0·81). Data were collected for $h \geq 0$, $k \geq 0$ and all l (maximum $h, k, l = 12$, 7 and 14, respectively). Three standards were monitored every 100 reflections with variation within counting statistics. Scan speeds range from 5·86 to 29·30° min^{-1}, 941 total reflections (out to $2\theta = 40°$); 827 unique reflections; 701 reflections with $F > 3\sigma(F)$. The structure was solved *via* direct methods, yielding copper and chlorine positions. The pyridinium ring was found on the subsequent difference map. Final refinement on F for all observed reflections with anisotropic thermal parameters for the non-hydrogen atoms gave $R = 0{\cdot}054$ and $wR = 0{\cdot}060$ based on 97 least-squares parameters, with an average $|\Delta/\sigma| = 0{\cdot}012$ (*SHELXTL*; Sheldrick, 1983), with $w^{-1} = [\sigma^2(F_o) + g|F_o|^2]$, $g = 0{\cdot}0012$. The goodness of fit was equal to 1·49. Hydrogen atoms were fixed at calculated positions ($r_{C-H} = r_{N-H} = 0{\cdot}96$ Å) with isotropic thermal parameters approximately 20% larger than those of the corresponding heavy atom. The largest residual on the final difference map was 0·3 e Å^{-3} near the copper atom, the largest negative residual being −0·5 e Å^{-3}. Scattering factors, corrected for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974).

The tetrabromide crystals were very dark brown/red plates, which crystallized out of an aqueous solution of 2-amino-5-methylpyridinium bromide, with excess copper bromide (approx. 1:4 stoichiometry). The crystals were redissolved in a minimum of water and excess 1·0*M* copper bromide added. The recrystallized product was similar in appearance to the first set of crystals. A triangular crystal approximately 0·1 × 0·1 × 0·1 mm on the triangular edges and about 0·05 mm thick was selected for data collection. Data were collected on a Nicolet *R*3*m*/*E* diffractometer as described above. Agreement between equivalent reflections was 0·0234. The monoclinic cell and orientation matrix were defined by least-squares refinement of 25 reflections in the 2θ range 30–32°. Space group *C*2/*c* (extinctions *hkl*, *h* + *k* odd; *h*0*l*, *l* odd). Empirical absorption corrections ($\mu = 94{\cdot}46$ cm^{-1}) assuming an ellipsoidal crystal (minimum transmission 0·039, maximum transmission 0·071). Data were collected for $h \geq 0$, $k \geq 0$ and all l (maximum $h, k, l = 12$, 9 and 14, respectively). Three standards were monitored every 100 reflections with variation within counting statistics. Scan speeds ranged from 4·00° min^{-1} to 29·30° min^{-1}. 940 total reflections (out to $2\theta = 40°$), with 892 unique reflections and 658 reflections with $F > 3\sigma(F)$. The structure was solved *via* direct methods yielding the bromine and copper positions. The pyridinium ring was found on the subsequent difference map. Final refinement on F for all observed reflections with anisotropic thermal parameters for the non-hydrogen atoms with hydrogen atoms again fixed at calculated positions gave $R = 0{\cdot}052$ and $wR = 0{\cdot}049$ based on 96 least-squares parameters with an average $\Delta/\sigma = 0{\cdot}001$. Weighting scheme as above. The goodness of fit was 1·326. The largest residual on the difference map was 0·6 e Å^{-3} near the Cu(1) atom, the largest negative residual being −0·6 e Å^{-3}. Final positional parameters for the two compounds are given in Tables 1 and 2 with selected bond distances and angles reported in Tables 3 and 4.*

Discussion. The chloride salt contains discrete 2-amino-5-methylpyridinium cations (Fig. 1*a*) and isolated $CuCl_4^{2-}$ anions (Fig. 1*b*). N—H···Cl hydrogen bonds bind the ions together in the lattice, as seen in Fig. 2. Distances and angles within the cations are normal. The pyridine N—H moiety forms a short hydrogen bond with Cl(2), H(1)—Cl(2) = 2·84 (1), N(1)—Cl(2) = 3·25 (1) Å, while the amino hydrogens form bifurcated hydrogen bonds to surrounding Cl(1)

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43723 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and Cl(2) atoms; H—Cl distances range from 2·78 to 3·02 Å, N(7)—Cl distances range from 3·54 (1) to 3·62 (1) Å.

Within the $CuCl_4^{2-}$ anion, the Cu—Cl bond distances average 2·240 Å. The anion has approximate D_{2d} symmetry, and assumes a geometry intermediate between tetrahedral and square planar. The extent of distortion can be characterized by the *trans* Cl—Cu—Cl angles, θ, which average 140° in this salt (*cf.* 109·5° in tetrahedral geometry, 180° in square-planar geometry), or by the dihedral angle, β, between $CuCl_2$

Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters* (Å^2 ×10^3) *for the tetrachlorocuprate*

Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cl(1)	4066 (2)	1059 (3)	3491 (2)	65 (1)
Cl(2)	3711 (2)	782 (3)	6644 (2)	62 (1)
Cu(1)	5000	57 (2)	2500	45 (1)
N(1)	1213 (6)	2488 (8)	9437 (5)	56 (3)
C(2)	1711 (6)	1347 (11)	9059 (6)	45 (4)
C(3)	1882 (7)	−89 (12)	9493 (7)	56 (4)
C(4)	1542 (7)	−241 (11)	10299 (7)	54 (4)
C(5)	1025 (6)	946 (12)	10665 (6)	47 (3)
C(6)	865 (7)	2299 (12)	10225 (6)	53 (4)
N(7)	2013 (6)	1609 (10)	8290 (5)	66 (3)
C(8)	652 (8)	764 (12)	11524 (6)	62 (4)

Table 2. *Atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3) *for the tetrabromocuprate*

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Br(1)	4036 (1)	1091 (2)	3526 (1)	70 (1)
Br(2)	3675 (1)	898 (2)	6594 (1)	66 (1)
Cu(1)	5000	17 (3)	2500	52 (1)
N(1)	1225 (10)	2493 (15)	9445 (9)	59 (6)
C(2)	1684 (11)	1404 (20)	9072 (11)	49 (7)
C(3)	1809 (12)	−11 (18)	9466 (12)	58 (7)
C(4)	1494 (12)	−194 (19)	10263 (11)	62 (7)
C(5)	1033 (11)	968 (21)	10665 (10)	52 (6)
C(6)	889 (11)	2287 (21)	10250 (11)	59 (7)
N(7)	1972 (10)	1679 (17)	8297 (9)	76 (6)
C(8)	702 (13)	750 (21)	11540 (9)	75 (8)

Table 3. *Bond distances* (Å) *and angles* (°) *for the* $CuCl_4^{2-}$ *anion*

Cu—Cl(1)	2·233 (3)	Cl(1)—Cu—Cl(2)	97·4 (1)
Cu—Cl(2)	2·247 (2)	Cl(1)—Cu—Cl(1*a*)	136·0 (1)
		Cl(1)—Cu—Cl(2*a*)	96·0 (1)
		Cl(2)—Cu—Cl(2*a*)	143·7 (1)

Table 4. *Bond distances* (Å) *and angles* (°) *for the* $CuBr_4^{2-}$ *anion*

Cu—Br(1)	2·369 (2)	Br(1)—Cu—Br(2*a*)	98·5 (1)
Cu—Br(2)	2·385 (2)	Br(1)—Cu—Br(1*a*)	133·4 (2)
		Br(1)—Cu—Br(2*b*)	96·7 (1)
		Br(2*a*)—Cu—Br(2*b*)	140·9 (2)

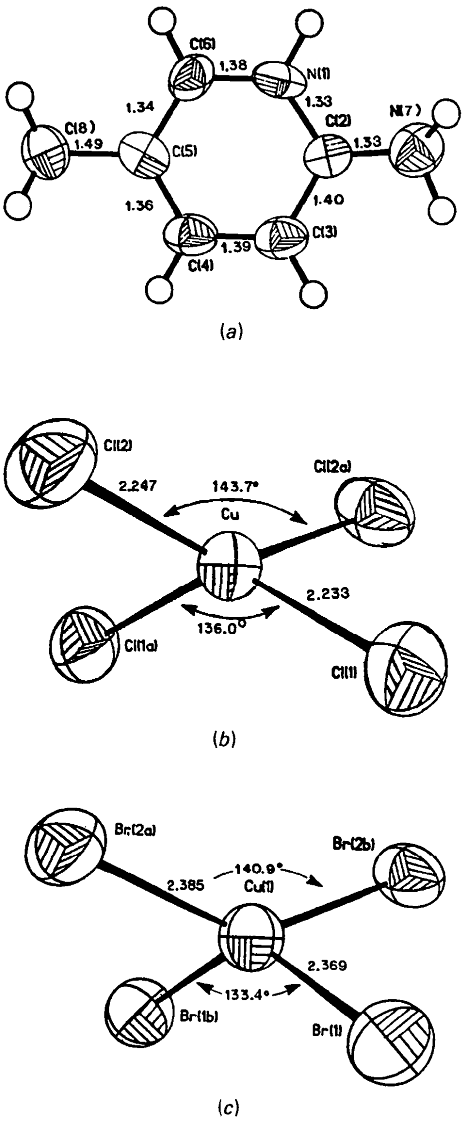

Fig. 1. (*a*) The 2-amino-5-methylpyridinium cation in $(C_6H_9N_2)_2$-$CuCl_4$ with selected bond distances (Å). (*b*) The $CuCl_4^{2-}$ anion. (*c*) The $CuBr_4^{2-}$ anion in the bromide salt.

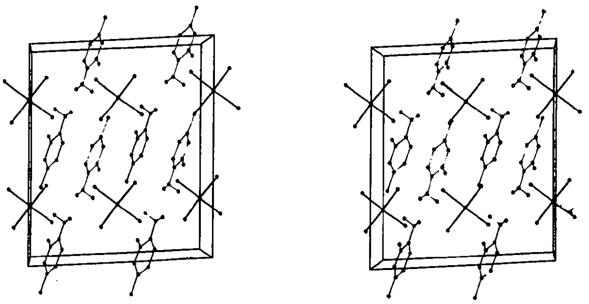

Fig. 2. Packing diagram of the structure of $(C_6H_9N_2)CuCl_4$. For clarity, only the hydrogens bonded to the nitrogen atoms are shown. The *a* axis is horizontal and the *c* axis vertical.

planes which is 54·5° (90° for tetrahedral, 0° for square planar). Previously studied CuCl$_4^{2-}$ anions have shown a variable range of values from $\theta = 124^\circ$ and $\beta = 67{\cdot}9^\circ$ in Cs$_2$CuCl$_4$ (Helmholz & Kruh, 1952) to $\theta = 180^\circ$ and $\beta = 0^\circ$ in bis(*N*-methylphenethylammonium)CuCl$_4$ (Harlow, Wells, Watt & Simonsen, 1974). This distortion of geometry has been associated with a monotonic variation in the *d–d* transition energies (Willett, Haugen, Lebsack & Morrey, 1974; Battaglia, Bonamartini-Corradi, Marcotrigiano, Menabue & Pellacani, 1979) and the electronic structure of the ion (Solomon, Hare, Dooley, Dawson, Stephens & Gray, 1980). The role of hydrogen bonding in stabilizing the square-planar configuration through removal of charge from the chloride ion has been argued (Geiser & Willett, 1984). Thus, with weak hydrogen bonding electrostatic forces dominate, yielding a geometry close to tetrahedral, while with strong hydrogen bonding the crystal field stabilization energy dominates, giving a geometry closer to square planar.

The tetrabromide structure is analogous to that of the tetrachloride (Fig. 1*c*). The cation bond angles and distances were within two standard deviations of those obtained for the chloride salt. The only significant difference lies in the Cu—Br *vs* Cu—Cl distance (average) of 2·377 (1) *vs* 2·240 (1) Å and the *trans* Br—Cu—Br angle *vs* the Cl—Cu—Cl angle of 137 (1) *vs* 140 (1)°. The compression of the coordination sphere towards tetrahedral geometry is as expected upon replacement of the chloride ions by the larger bromide ion.

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Structure of *cis*-Dichlorobis(dimethylphenylphosphine)platinum(II)

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Abstract. $[\mathrm{PtCl_2(C_8H_{11}P)_2}]$, $M_r = 542{\cdot}3$, triclinic, $P\bar{1}$, $a = 9{\cdot}127$ (2), $b = 10{\cdot}286$ (3), $c = 10{\cdot}890$ (2) Å, $\alpha = 74{\cdot}40$ (2), $\beta = 70{\cdot}24$ (2), $\gamma = 88{\cdot}23$ (2)°, $V = 924{\cdot}7$ (4) Å^3, $Z = 2$, $D_x = 1{\cdot}947$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 81{\cdot}2$ cm^{-1}, $F(000) = 520$, $T = 294$ K, $R = 0{\cdot}026$ for 4693 unique observed reflections. The average Pt—P and Pt—Cl distances are 2·244 (2) and 2·357 (3) Å, respectively.

Introduction. During investigation of insertion reactions in Pt$^{\mathrm{II}}$ σ-allyl complexes, we had the opportunity of obtaining crystals of the title compound. The structure was determined in order to obtain further insight into the electronic and steric effects of phosphine ligands.

Experimental. Crystal approximately 0·11 × 0·32 × 0·50 mm. Weissenberg and precession photographs indicated the crystal to be triclinic. Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation; lattice parameters refined by least-squares fit of 25 reflections in the range $17 < \theta < 21^\circ$. Intensity data measured by the $\omega/2\theta$ scan technique, ω scan angle = $(1{\cdot}3 + 0{\cdot}35\tan\theta)^\circ$; variable scan rate, 0·9–5° min^{-1}. Three standard reflections ($\bar{7}\bar{4}\bar{4}$, $\bar{7}40$, $\bar{7}4\bar{5}$), monitored every 3000 s, showed no decay throughout

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